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APPLICATION FOR UNITED STATES LETTERS PATENT

FOR

LOW SULFUR, LOW ASH, AND LOW PHOSPHORUS LUBRICANT ADDITIVE PACKAGE USING AN ALKYLAMINE SALT OF A DIALKYLMONOTHIOPHOSPHATE

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Inventor: Carl Esche

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to lubricating oil compositions, their method of preparation, and use. More specifically, this invention relates to an oil soluble lubricating additive package to achieve low sulfur, low ash, and low phosphorus levels in fully formulated oil.

BACKGROUND OF THE INVENTION

[0002] Combustion engines generate emissions that can pollute our environment. In response to increasing regulation and environmental concerns, engine manufacturers have recognized the need to reduce engine emissions. In an effort to reduce emissions in exhaust gases, manufacturers have used particulate traps and catalytic converters. However, the lubricating oil used in the engine is oftentimes detrimental to devices such as catalytic converters or particulate traps. For example, phosphorus present in the lubricating oil is believed to interfere with catalytic efficiency. Further, it is believed that sulfur present in the lubricating oil, after oxidation and neutralization, may form sulfates that plug exhaust gas traps thereby preventing them from oxidizing and burning off trapped organic particulate matter. Accordingly, engine manufacturers are requiring lubricating oils that have lower and lower sulfur, ash, and phosphorus levels.

SUMMARY OF THE INVENTION

[0003] An object of the present invention is to provide an oil soluble lubricating additive package that can be used to formulate a low sulfur, low ash, and low phosphorus content oil for use in either gasoline or diesel engines. Further, a second object of the present invention is to provide lubricating oils that contain minimal sulfur, ash, and phosphorus levels.

[0004] Additionally, another goal of the present invention is to provide a method for lubricating the moving parts of a machine.

[0005] The present invention provides for an oil soluble lubricant additive package comprising (1) at least one alkylamine salt of a dialkylmonothiophosphate, and (2) at least one detergent, wherein the weight ratio of the alkylamine salt of a dialkylmonothiophosphate to the detergent is from about 0.05:1 to about 3:1.

[0006] In an embodiment the oil soluble lubricant additive package of the present invention has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt%.

[0007] In an embodiment at least one of the at least one detergent is selected from the group consisting of calcium sulfonate, magnesium sulfonate, sodium sulfonate, non-sulfurized Mannich phenates, sulfurized phenates, salicylates, overbased salicylates, saligenin, overbased saligenin, overbased carboxylic acids, and combinations thereof.

[0008] The present invention additionally includes a lubricating oil comprising the inventive oil soluble lubricant additive package, having a total base number of less than about 10, and at least one property selected from the group consisting of: a

sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

[0009] The present invention additionally includes machines lubricated by the lubricating oil described above. Although the machine may be any machine for which the inventive lubricating oil would provide satisfactory lubrication, it is envisioned that such machinery would include gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes. Furthermore, the present invention includes vehicles comprising the inventive oil soluble lubricant additive package described above.

[0010] The present invention also includes a method for lubricating an engine crankcase comprising the step of: at least partially filling the crankcase with a lubricant comprising the oil soluble lubricant additive package described above.

[0011] Further, the present invention provides a method for lubricating moving parts of a machine comprising the step of: contacting at least one moving part with a lubricant comprising the oil soluble lubricant additive package described above. Although the method may be successfully employed on a wide variety of machines, it is envisioned that such machinery would include: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0012] The present invention provides a second inventive oil soluble lubricant additive package comprising: (1) at least one alkylamine salt of a dialkylmonothiophosphate and (2) at least one dispersant, wherein the weight ratio of the alkylamine salt of a dialkylmonothiophosphate to the dispersant is from about 1:4 to about 1:20.

[0013] In another embodiment the oil soluble lubricant additive package described above has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt%.

[0014] It is also useful herein that at least one dispersant used in the oil soluble lubricant additive package described above has a molecular weight of from about 1,000 to about 20,000 amu. In one embodiment the at least one dispersant is a maleic anhydride functionalized polyisobutylene polymer that has been reacted with a polyamine. Also the at least one dispersant can be a product of a Mannich reaction. It is further equally possible that the at least one dispersant is an ethylene-propylene type dispersant.

[0015] It is further preferred in one embodiment that the oil soluble lubricant additive package described above additionally comprise at least one component selected from the group consisting of: viscosity index improvers and pour point depressants.

[0016] It is additionally useful herein that a lubricating oil comprising the oil soluble lubricant additive package described above has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%. In one embodiment the ash content of the lubricating oil is less than about 1.0 wt% and in another embodiment is less than about 0.8 wt%.

[0017] The present invention also includes machines lubricated by the lubricating oil described above. Although the inventive lubricating oil can be used on a wide variety of machines, it is envisioned that the machines especially suited for

lubrication include: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0018] Additionally, the present invention includes vehicles comprising the oil soluble lubricant additive package described above.

[0019] The present invention additionally includes a method for lubricating an engine crankcase comprising the step of: at least partially filling the crankcase with a lubricant comprising the oil soluble lubricant additive package described above.

[0020] A method for lubricating moving parts of a machine is also provided comprising the step of: contacting at least one moving part with a lubricant comprising the oil soluble lubricant additive package described above. Although the method may be employed with a wide variety of machines, it is believed that the method is especially suited for use with: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0021] The present invention additionally provides for an oil soluble lubricating additive package comprising: (1) at least one alkylamine salt of a dialkylmonothiophosphate; and (2) at least one antioxidant, wherein the weight ratio of the alkylamine salt of a dialkylmonothiophosphate to antioxidant is from about 10:1 to about 1:5.

[0022] It is preferred that the oil soluble lubricant additive package has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt%.

[0023] It is preferred that at least one antioxidant used in the oil soluble lubricant additive package of the present invention is selected from the group consisting of:

alkylated diphenylamines, sulfurized olefins, phenols, hindered phenols, and sulfurized phenols.

[0024] The present invention also provides for a lubricating oil comprising the oil soluble lubricant additive package described above, having a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%. In one embodiment the ash content of the lubricating oil is less than about 1.0 wt% and in another embodiment is less than about 0.8 wt%.

[0025] The present invention also includes machines lubricated by the lubricating oil described above. Although a wide variety of machines may be lubricated by the present inventive lubricating oil, it is preferred that the machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0026] Additionally, the present invention includes vehicles comprising the oil soluble lubricant additive package described above.

[0027] The present invention also includes a method for lubricating an engine crankcase comprising the step of: at least partially filling the crankcase with a lubricant comprising the oil soluble lubricant additive package described above.

[0028] The present invention additionally provides a method for lubricating moving parts of a machine comprising the step of: contacting at least one moving part with a lubricant comprising the oil soluble lubricant additive package described above. It is envisioned that this method may be employed with a wide variety of machines including: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0029] The present invention additionally provides yet another oil soluble lubricant additive package comprising: (1) at least one alkylamine salt of a dialkylmonothiophosphate; (2) and at least one component selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.

[0030] It is preferred that the oil soluble lubricant additive package described above has at least one property selected from the group consisting of: a sulfur content less than about 3 wt% and a phosphorus content less than about 1.2 wt%.

[0031] It is preferred that the oil soluble lubricant additive package is essentially free of non-sulfurized Mannich phenate.

[0032] It is further preferred that a lubricating oil comprising the oil soluble lubricant additive package described above, has a total base number of less than about 10 mg KOH/g, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%. In one embodiment the ash content of the lubricating oil is less than about 1.0 wt% and in another embodiment is less than about 0.8 wt%.

[0033] The present invention includes machines lubricated by the lubricating oil described above. Although it is envisioned that a wide variety of machines may be lubricated by the inventive lubricating oil described herein, it is preferred that the machines is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0034] The present invention also includes vehicles comprising the oil soluble lubricating additive package described herein.

[0035] The present invention also provides a method for lubricating an engine crankcase comprising the step of: at least partially filling the crankcase with a lubricant comprising the oil soluble lubricant additive package described above.

[0036] The present invention additionally provides a method for lubricating the moving parts of a machine comprising the step of: contacting at least one moving part with a lubricant comprising the oil soluble lubricant additive package described above.

[0037] The present invention also provides a method of achieving a low sulfur, low ash, and low phosphate oil formulation comprising: (1) providing an oil soluble lubricant additive package comprising an alkylamine salt of a dialkylmonothiophosphate; and (2) admixing the oil soluble lubricant additive package with at least a base oil so as to form a lubricating oil having a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%. In one embodiment the ash content of the lubricating oil is less than about 1.0 wt% and in another embodiment is less than about 0.8 wt%.

[0038] It is preferred that the lubricating oil additionally comprises at least one additive selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0039] In accordance with the foregoing summary, the following presents a detailed description of the preferred embodiment of the invention that is currently considered to be the best mode.

[0040] We begin with a discussion of the various components employed in the present invention. Then we shall present an example of an oil formulation based upon the oil soluble additive package of the present invention. Finally, we conclude with a comparison of an inventive oil formulation against a control formulation in the CAT 1N engine test.

BASE OIL

[0041] The base oils useful herein include natural lubricating oils, synthetic lubricating oils and mixtures thereof. Suitable lubricating oils also include basestocks obtained by isomerization of synthetic wax and slack wax, as well as basestocks produced by hydrocracking the aromatic and polar components of the crude. In general, both the natural and synthetic lubricating oils will each have a kinematic viscosity ranging from about 1 to about 40 mm^2/s (cSt) at 100° C, although typical applications will require each of the base oils to have a viscosity ranging from about 1 to about 12, preferably 2 to 8, mm^2/s (cSt) at 100° C.

[0042] Natural lubricating oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural lubricating oil is mineral oil.

[0043] The mineral oils useful in this invention can include but are not limited to all common mineral oil base stocks. This would include oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, etc. They may be hydrotreated or hydrorefined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be produced from natural crude sources or be

composed of isomerized wax materials or residues of other refining processes. In one embodiment, the oil of lubricating viscosity is a hydrotreated, hydrocracked and/or iso-dewaxed mineral oil having a Viscosity Index (VI) of greater than 80, preferably greater than 90; greater than 90 volume % saturates and less than 0.03 wt. % sulfur.

[0044] Group II and Group III basestocks are also particularly suitable for use in the present invention, and are typically prepared from conventional feedstocks using a severe hydrogenation step to reduce the aromatic, sulfur and nitrogen content, followed by dewaxing, hydrofinishing, extraction and/or distillation steps to produce the finished base oil. Group II and III basestocks differ from conventional solvent refined Group I basestocks in that their sulfur, nitrogen and aromatic contents are very low. As a result, these base oils are compositionally very different from conventional solvent refined basestocks. The American Petroleum Institute has categorized these different basestock types as follows: Group I, >0.03 wt. % sulfur, and/or <90 vol% saturates, viscosity index between 80 and 120; Group II, ≤ 0.03 wt. % sulfur, and ≥ 90 vol% saturates, viscosity index between 80 and 120; Group III, ≤ 0.03 wt. % sulfur, and ≥ 90 vol% saturates, viscosity index > 120; Group IV, poly-alpha-olefins. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulfur and aromatics content, generally fall into the Group II and Group III categories.

[0045] There is no limitation as to the chemical composition of the various basestocks used in the present invention. For example, the proportions of aromatics, paraffinics, and naphthenics in the various Group I, Group II and Group III oils can vary substantially. The degree of refining and the source of the crude used to produce the oil generally determine this composition. In one embodiment, the base oil comprises a mineral oil having a VI of at least 110.

[0046] The lubricating oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oil breakdown products.

[0047] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymerized olefins; alkylbenzenes; polyphenyls; and alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof, and the like. Preferred synthetic oils are oligomers of α-olefins, particularly oligomers of 1-decene, having a viscosity ranging from about 1 to about 12, preferably 2 to 8, mm^2/s (cSt) at 100° C. These oligomers are known as poly-α-olefins or PAOs.

[0048] Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is

exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polypropylene glycol having a molecular weight of 100-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3-C_8 fatty acid esters, and C_{12} oxo acid diester of tetraethylene glycol).

[0049] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, subric acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl isothalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebasic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like. A preferred type of oil from this class of synthetic oils is adipates of C_4 to C_{12} alcohols.

[0050] Esters useful as synthetic lubricating oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaeythritol, dipentaerythritol, tripentaerythritol, and the like.

[0051] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetra-ethyl silicate, tetra-isopropyl silicate, tetra-(2-

ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-*tert*-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes and poly (methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus containing acids (e.g., tricresyl phosphate, trioctylphosphate, and diethyl ester of decylphosphonic acid), polymeric tetra-hydrofurans, poly-alpha-olefins, and the like.

VISCOSITY INDEX IMPROVERS

[0052] Viscosity index improvers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity index improvers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity index improvers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6, preferably 10^4 to 10^6, as determined by gel permeation chromatography or osmometry.

[0053] The viscosity index improvers useful herein can include polymethacrylate-based ones, olefin copolymer-based ones, (e.g., isobutylene-based and ethylene-propylene copolymer based ones), polyalkyl styrene-based ones, hydrogenated styrene-butadiene copolymer-based ones, and styrene-maleic anhydride ester copolymer-based ones.

[0054] Representative examples of suitable viscosity index improvers are found in U.S. Pat. Nos. 5,075,383; 5,102,566; 5,139,688; 5,238,588; and 6,107,257. The above references are incorporated herein by reference.

POUR POINT DEPRESSANTS

[0055] Pour point depressants are used to improve low temperature properties of oil-based compositions. See, for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lezius Hiles Co. publishers, Cleveland, Ohio, 1967). Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and ter-polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants are described in U.S. Patent Nos. 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715, which are herein incorporated by reference for their relevant disclosures.

DISPERSANTS

[0056] Dispersants used in the present invention may be ash-producing or ashless. Suitable dispersants for use herein can typically comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone via a bridging group. The dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono- and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine, and Koch reaction products. The long chain aliphatic hydrocarbons can be polymers such as polyalkylenes, including, for example, polyisobutylene, polyethylene, polypropylene, and copolymers thereof and/or copolymers with other alpha-olefins. Typical PIB molecular weights useful herein can range from about 950 to 6000.

[0057] Representative examples of dispersants suitable for use in the present invention are found in U.S. Patent Nos. 5,075,383; 5,139,688; 5,238,588; and 6,107,257. Additional representative examples are found in U.S. Patent Application Publication No. 2001/0036906A1. The disclosures of the afore-mentioned references are incorporated herein by reference.

DETERGENTS

[0058] A detergent is an additive that reduces the formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines. Detergents typically possess acid-neutralizing properties and are capable of keeping finely divided solids in suspension. Metal detergents are used preferably for improving the acid-neutralizing properties, high-temperature detergency, and anti-wear properties of the resulting lubricating oil composition.

[0059] Detergents used herein may be any detergent used in lubricating oil formulations, and may be of the ash-producing or ashless variety. Detergents suitable for use in the present invention include all of the detergents customarily used in lubricating oils, including metal detergents. Specific examples of metal detergents are those selected from alkali metal or alkaline earth metal sulfonates, alkali metal or alkaline earth metal phenates, and alkali metal or alkaline earth metal salicylates. In an embodiment, the lubricating oil formulation is essentially free of sulfurized phenate detergent.

[0060] Representative examples of suitable detergents useful in the present invention are found in U.S. Pat. Nos. 6,008,166. Additional representative examples of suitable detergents are found in U.S. Patent Application Nos. 2002/0142922A1, 2002/0004069A1, and 2002/0147115A1. The disclosures of the afore-mentioned references are incorporated by reference herein.

ALKYLAMINE SALT OF A DIALKYLMONOTHIOPHOSPHATE

[0061] Although any oil soluble alkylamine salt of a dialkylmonothiophosphate that imparts suitable anti-wear performance to the finished oil may be used in the present invention, a synthesis method for a preferred alkylamine salt of a dialkylmonothiophosphate for use in the present invention follows.

[0062] In a round bottom flask equipped with a thermocouple, stirrer, addition funnel and condenser is charged 148.50 grams of ARMEEN OL. An effective amount of di-n-butyl hydrogen phosphite (DBHP) is charged to the addition funnel. Begin vigorous stirring of the ARMEEN OL and charge an effective amount of elemental sulfur to the reactor. After the sulfur addition is complete, immediately begin adding the DBHP dropwise to the reactor. The reaction temperature should not exceed 70 °C. The temperature can be adjusted by the rate of DBHP addition. The DBHP is charged over four hours. The reaction should be monitored for DBHP buildup by taking an IR each hour and checking the IR for unreacted DBHP. After the DBHP addition is complete, charge the n-octylamine (13.29 grams). Heat the reaction for 30 minutes at 50 °C.

[0063] ARMEEN OL is a commercial product from AKZO Nobel. ARMEEN OL is a primary oleyl amine. Other amines supplied by AKZO Nobel suitable for this invention include ARMEEN 12D, ARMEEN 16D, ARMEEN 18D, ARMEEN O, ARMEEN OD, ARMEEN OLD, ARMEEN C, ARMEEN S, and ARMEEN SD. Any primary, secondary or tertiary amine is suitable as long as the final product is oil soluble and it imparts suitable anti-wear performance to an oil.

[0064] The alykl groups on the phosphite and/or phosphate can be of any length as long as the final product is oil soluble and it imparts suitable anti-wear performance to an oil.

ANTIOXIDANTS

[0065] Useful antioxidant materials include oil soluble phenolic compounds, oil soluble sulfurized organic compounds, oil soluble amine antioxidants, oil soluble organo borates, oil soluble organo phosphites, oil soluble organo phosphates, oil soluble organo dithiophosphates and mixtures thereof. Such antioxidants can be metal free (that is, free of metals which are capable of generating sulfated ash), and therefore are most preferably ashless (having a sulfated ash value not greater than 1 wt. % SASH, as determined by ASTM D874).

[0066] Representative examples of suitable antioxidants useful in the present invention are found in U.S. Patent No. 5,102,566. Additional representative examples of suitable antioxidants useful in the present invention are found in U.S. Patent Application Publication No. 2001/0012821A1. The disclosures of the aforementioned references are incorporated by reference herein.

FRICTION MODIFIERS

[0067] Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions.

[0068] Friction modifiers include such compounds as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amines, aliphatic carboxylic acids, aliphatic carboxylic esters of polyols such as glycerol esters of fatty acid as exemplified by glycerol phenate, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

Additionally suited for use in the present invention are friction modifiers containing molybdenum.

[0069] Representative examples of molybdenum-containing friction modifiers include those found in U.S. Patent Nos. 5,650,381; RE37,363E; 5,628,802; 4,889,647; 5,412,130; 4,786,423; 4,812,246; 5,137,647; 5,364,545; 5,840,672; 5,925,600; 5,962,377; 5,994,277; 6,017,858; 6,150,309; 6,174,842; 6,187,723; 6,268,316; European Patent Nos. EP 222 143 B1; EP 281 992 B1; EP 719 314 B1; EP 719 315 B1; EP 874 040 A1; EP 892 037 A1; EP 931 827 A1; EP 1 041 134 A1; EP 1 041 135 A1; EP 1 087 008 A1; EP 1 088 882 A1; EP; Japanese Patent No. JP 11035961; and International Publication Nos. WO 95/07965; WO 00/08120; WO 00/71649.

[0070] Representative examples of suitable friction modifiers are found in U.S. Pat. Nos. 3,933,659; 4,105,571; 3,779,928; 3,778,375; 3,852,205; 3,879,306; 3,932,290; 3,932,290; 4,028,258; 4,344,853; 5,102,566; 6,103,674; 6,174,842; 6,500,786; 6,500,786; and 6,509,303. Additional representative examples of suitable friction modifiers are found in U.S. Patent Application Publication No. 2002/0137636 A1. The disclosures of the above references are incorporated herein by reference.

CAT 1N ENGINE TEST RESULTS

[0071] The CAT 1N engine test is a commonly used test for evaluating the acceptability of heavy-duty diesel engine oils for Caterpillar engines. The test employs a single cylinder aluminum piston diesel engine. The acceptability of an oil formulation is based upon the following parameters: average oil consumption, piston deposits, % top groove fill, % top land heavy carbon. Further, in order to pass the CAT 1N diesel test, no stuck pistons, piston rings or liner distress is permitted.

[0072] To determine the efficacy of the inventive additive, a control formulation comprising a zinc dialkyldithiophosphate was compared to a formulation wherein the zinc dialkyldithiophosphate was replaced by an alkylamine salt of a dialkylmonothiophosphate with a compensating reduction in the amount of base oil. Detergent #1 is a metal sulfonate and detergent #2 is a commercially available metal salicylate detergent. In this example, the weight ratio of alkylamine salt of a dialkylmonothiophosphate to combined detergents is 0.675 to 1.45 or about 1:2.14.

Composition, wt% basis	Control Formulation	Inventive Formulation
Base Oil #1	52.00	51.575
Base Oil #2	27.00	27.00
Viscosity Index Improver	8.50	8.50
Pour Point Depressant	0.20	0.20
Dispersant #1	3.00	3.00
Dispersant #2	5.03	5.03
Detergent #1	0.50	0.50
Detergent #2	0.95	0.95
Alkylamine salt of a dialkylmonothiophosphate	0.00	0.675
Zinc Dialkyldithiophosphate	0.25	0.00
Antioxidant #1	0.50	0.50
Antioxidant #2	0.50	0.50
Anti-Foaming Agent	0.01	0.01
Friction Modifier	0.50	0.50
Process Oil	1.06	1.06
Kinematic Viscosity @ 100°C	13.79 centistoke	13.17 centistoke

[0073] The following table compares the control formulation's performance against the inventive formulation. The column marked "Test #1" provides the pass/fail limits for the CAT 1N test for a single trial. If a given oil formulation does not provide satisfactory results with a single trial, multiple trials may be averaged together and this average compared against the corresponding pass/fail limits for the number of tests being averaged. That is to say, if two trials of the inventive formulation were

averaged together, the averaged results would be compared against the pass/fail limits provided in the "Test#2" column.

	Control Formulation	Inventive Formulation	Test #1	Test #2	Test #3
TLHC, %	0	0	3	4	5
TGF, %	9	9	20	23	25
WD	260.9	235.2	286.2	311.7	323
O.C., avg	0.205	0.201	0.5 max (0 - 252 hour)		
O.C.E.O.T.	0.21	0.212	No scuffing		

TLHC, % - Top Land Heavy Carbon
TGF, % - Top Groove Fill
WD - Weight of Deposit
O.C. - Oil Consumption
O.C.E.O.T. - Oil Consumption at End of Test

[0074] As can be seen from the table above, the inventive formulation performed well in the CAT 1N test. The inventive formulation did not require additional trials, as single trial performance was satisfactory. The inventive formulation exhibited a marked reduction in weight of deposit. These results demonstrate the improved performance imparted to the formulated oil by the substitution of an alkylamine salt of a dialkylmonothiophosphate for zinc dialkyldithiophosphate.

[0075] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiment(s), but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims, which are incorporated herein by reference.